EXAMINATION OF CRUST LEATHER FOR RESIDUALS FROM A POTENTIAL HIDE PRESERVATIVE

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Abstract

Potassium dimethyldithiocarbamate (KDMDC) is a commercially available antimicrobial preservative registered by EPA for a variety of uses. This chemical has potential as an adjunct to brine curing for the preservation of cattlehides. KDMDC added to a brine raceway would permeate the hide during hide curing. This research was performed to determine whether or not this chemical could persist in the leather produced from brine-cured hides. It is theoretically possible that residual KDMDC in leather products could be extracted by perspiration creating a potential health hazard for the user. KDMDC was applied at normal and four-times-recommended application levels during brine curing of cattlehides. The cured hides were processed into crust leather that were then extracted with synthetic perspiration solution and the leachate analyzed for KDMDC by HPLC. Residual KDMDC was not found in any of the samples examined.

Introduction

Brine curing of cattlehides alone does not always result in adequate preservation during long-term storage and transportation. A variety of chemicals is commercially available to be added to a hide at some stage to help delay the onset of deterioration of cured cattlehides during storage. Carbamates are a recognized class of microbicides with a variety of applications. Potassium dimethyldithiocarbamate (Figure 1) is an antimicrobial preservative currently registered for use in water-treatment systems, water-based paint, and pulp- and paper-mill systems. It also has potential for use as an adjunct for brine curing. Since this chemical would be absorbed by the cattlehide during the curing process it is theoretically possible that it could remain in the hide throughout the tanning process and be present in the final leather made from the hide. KDMDC in leather used in the manufacture of personal goods could potentially be extracted by perspiration from individuals wearing or using the leather product. Over a period of time this might be a potential health hazard. To investigate whether or not this possibility is of practical concern, leather was prepared from brine-cured hides treated with two different levels of KDMDC. These hides were processed through to dry crust in a pilot-plant tannery using a modification of the USDA standard process[1]. Samples of the crust leather were extracted with synthetic perspiration and the leachates analzyed for KDMDC by HPLC.

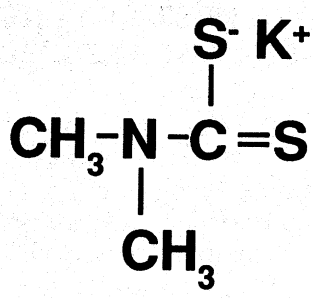

FIG. 1. — Chemical structure of Potassium Dimethyldithiocarbamate

Materials and Methods

Brine Curing of Cattlehides with KDMDC

Two steer hides were obtained within several hours of slaughter from a local abattoir. These hides were sided, fleshed and quartered in the pilot-plant tannery. The hide sections were divided into three groups that were labeled with a series of punched holes. Four sections were brine cured without the addition of KDMDC, two sections were brine cured with the commercially recommended level of KDMDC (Buckman Laboratories, Inc., Memphis, TN*) and four times the recommended level was applied to the final two sections. Each group was weighed, saturated brine was added at four times the weight of the hide samples, followed by the appropriate amount of KDMDC. The hide samples were cured overnight in a drum which ran 8 RPM for 5 min each hr for 18 hr. After curing the samples were stacked and drained overnight.

Conversion of Cattlehides to Leather

The brine-cured and treated hides were drum processed through to crust leather as follows. After an overnight soak a modified standard pilot-plant process for tanning cattlehides[1] was used to tan the samples. A 16 hr combination hairburn and lime was used in place of a separate four-hour hairburn followed by a 12 hr lime. The hides were then bated, pickled to pH 1.38, masked with 1 percent formate and tanned with 8 percent Tanolin R (Van Waters & Rogers, Salem, Mass.)* to pH 2.58. After tanning, the blue stock was horsed overnight and wrung the next morning. Texol 50 and Nutreen X (both from Salem Oil & Grease, Salem, Mass.)* were used for fatliquoring and retanning was done with Monotan R (Henkel, Saugus, Mass.)* The crust leather was toggle dried overnight at 90°F without splitting. Two-by-four inch samples of the dry crust were then cut out for KDMDC extraction analysis at Buckman laboratories in Memphis.

Extraction of KDMDC with Artificial Perspiration

Ten two-by-four-inch crust leather samples were cut from each treatment set. Leaching tests were done on each sample individually in petri dishes. Each sample was totally immersed in a solution of synthetic perspiration[2]. Five samples were soaked in synthetic perspiration solution for 4 hr and 5 were soaked in the same solution for 8 hr. During

*Reference to a brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

the soaking periods the individual swatches were periodically flexed to enhance the leaching of chemicals out of the hide.

Individual swatches were immersed in the synthetic perspiration solutions at 15 min intervals to facilitate the immediate analysis of the individual soaking solutions. Immediately after the soaking period was complete the leachate was transferred to a glass bottle and analyzed for KDMDC using HPLC.

Analysis of KDMDC by HPLC

Analysis of KDMDC was performed on a Perkin-Elmer Series 2 liquid chromatograph. The column used was 250 by 4.6 mm Supelcosil LC 18. The mobile phase was 62.5/37.5 acetonitrile/water containing 1.7 g $NiSO_4 \bullet H_2O$/liter. The KDMDC was detected at 320 nm using a Spectroflow 757 uv/vis detector. KDMDC was detectable at a level of 0.1 μg/mL. Ten-microliter sample volumes of leachate solution were injected daily into the column. A standard curve for KDMDC was prepared by analyzing aqueous standard solutions of KDMDC. A second standard curve was prepared in "synthetic perspiration" solution, in which KDMDC was stable.

Results

The leachates from each set of leather samples were analyzed for KDMDC. Samples of leachate were analyzed after 4 hr and after 8 hr of extraction. In every case KDMDC could not be detected at the detection limit (0.1 μg/mL) even after 8 hr of extraction. This corresponds to a calculated level of KDMDC in the leather of 300 ppb. Artificial-perspiration solutions did not interfere with the analysis of KDMDC. KDMDC, however, was found to be unstable in the leather leachates using the same artificial-perspiration solution. Four-hr leachates of the chrome-tanned leather samples from KDMDC-treated hides, which did not contain KDMDC according to previous analysis, were spiked with 0.08, 1.0, 4.0 and 10 μg/mL KDMDC. Immediately after the addition of KDMDC the samples were mixed and analyzed by HPLC. The results of this analysis for KDMDC are in Table 1. KDMDC was detected only in the samples spiked at levels of 4 and 10 μg/mL. In the two cases where KDMDC was detected, only 5 percent and 10 percent respectively of the original spike material was still present just minutes after the addition of the spike. It appears that there is a component of the chrome-tanned leather extracted by the perspiration solution that causes the rapid disappearance of KDMDC.

TABLE I

Stability of KDMDC in synthetic perspiration extracts of chrome tanned leather

Added KDMDC (μg/mL)	Extraction Time (hrs)	KDMDC Detected (μg/mL)
0.08	4	<0.1
1.0	4	<0.1
4.0	4	0.20
10.0	4	1.0

Discussion

The results of this study demonstrate that KDMDC could not be detected in synthetic-perspiration leachates of leather produced from cattlehides brine-cured with KDMDC. Since KDMDC is water soluble it may be washed out during beamhouse processing. Another possibility is that KDMDC might break down chemically during processing. The nitrogen-carbon bond in dimethyldithiocarbamate is unstable under acidic conditions and could hydrolyze to form a dimethylamine salt and carbon disulfide. (This condition exists during the pickle when the pH is reduced to below 2.) Finally, even if all the KDMDC was not washed out or hydrolyzed during processing, these experiments demonstrated that some component of chrome-tanned crust leather was extracted by synthetic-perspiration leachate causing rapid disappearance of the KDMDC.

Conclusions

Residual KDMDC was not detected in synthetic-perspiration leachates of leather prepared from cattlehides brine cured with added KDMDC. It is likely that the KDMDC is chemically or physically removed during processing. It can not be ruled out, however, that small amounts of KDMDC, if present in the final leather, might not be detectable in the synthetic leachate.

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